Electronic Supplementary Information

Halogen type as a selectivity switch in catalysed alkane oxyhalogenation

Guido Zichittella,[a] Begoña Puértolas,[a] Vladimir Paunović,[a] Theresa Block,[b] Rainer Pöttgen,[b] and Javier Pérez-Ramírez[a]*

[a] Institute for Chemical and Bioengineering, Department of Chemistry and Applied Biosciences, ETH Zurich, Vladimir-Prelog-Weg 1, 8093 Zürich, Switzerland.

[b] Institut für Anorganische und Analytische Chemie, Universität Münster, Corrensstrasse 30, 48149 Münster, Germany.

*Corresponding author. E-mail address: jpr@chem.ethz.ch

Table S1. Fitting parameters of ^{151}Eu Mössbauer spectroscopic measurements at 78 K.

Sample	Condition	Oxidation state	δ / mm s^{-1} [a]	ΔE_Q / mm s^{-1} [b]	Γ / mm s^{-1} [c]
Eu_2O_3	Precursor	Eu^{3+}	0.88 (2)	−3.50 (2)	3.10 (1)
EuOCl	Fresh	Eu^{3+}	0.62 (2)	2.50 (2)	2.64 (9)
	EOC	Eu^{3+}	0.78 (1)	1.50 (2)	2.70*
	POC	Eu^{3+}	0.65 (1)	2.10 (2)	2.84 (6)
EuOBr	Fresh	Eu^{3+}	0.81 (2)	2.50 (3)	2.70 (1)
	EOB	Eu^{3+}	0.79 (2)	2.70 (2)	2.50 (1)
	POB	82% Eu^{3+}	0.63 (1)	2.90 (1)	2.49 (7)
		18% Eu^{2+}	−13.93 (8)	4.70 (4)	2.70*

[a] isomer shift; [b] electric quadrupole splitting; [c] experimental line width; * parameters kept fixed during fitting; the standard deviation for each parameter is shown in brackets.

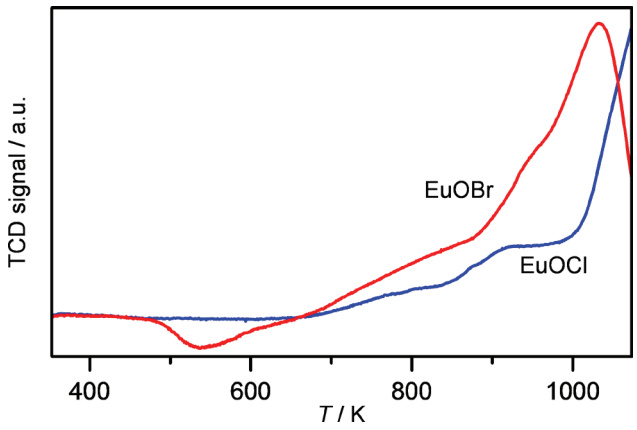

Fig. S1 Temperature-programmed reduction with H_2 of the fresh EuOCl and EuOBr catalysts.

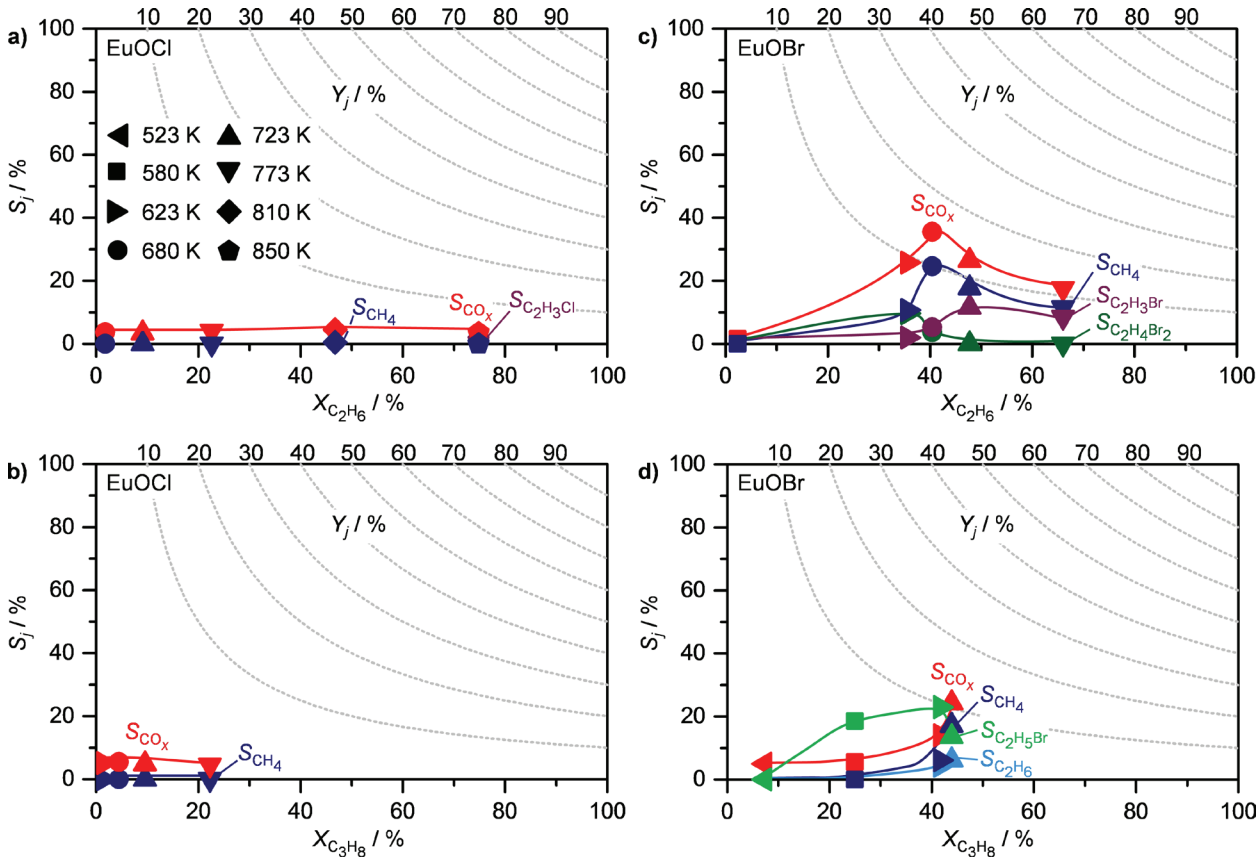

Fig. S2 Selectivity to product *j* as a function of the alkane conversion in the oxychlorination of **a)** ethane and **b)** propane and in the oxybromination of **c)** ethane and **d)** propane over the catalysts. The selectivity to the olefin and to the alkyl halide is shown in **Figure 1** of the main manuscript. The dotted grey lines denote the yield of product *j* and the different symbols refer to the reaction temperature.

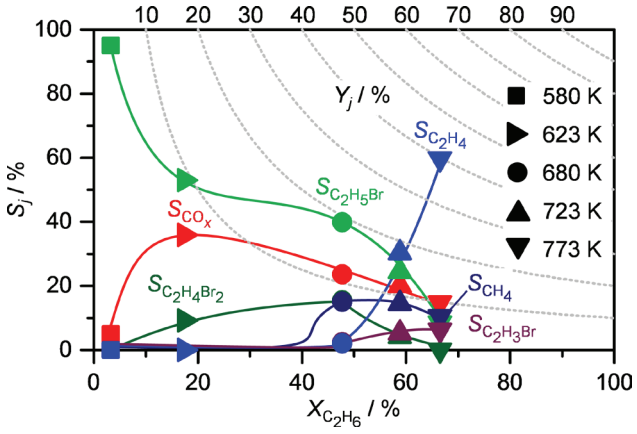

Fig. S3 Selectivity to product *j* as a function of the ethane conversion in the oxybromination of ethane over CeO_2. The dotted grey lines denote the yield of product *j* and the different symbols refer to the reaction temperature.

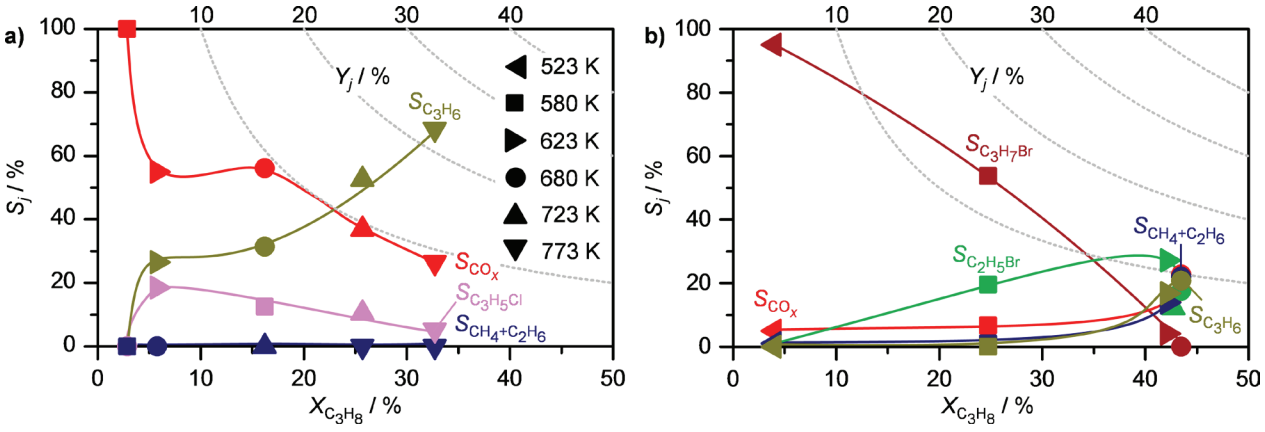

Fig. S4 Selectivity to product *j* as a function of the propane conversion in the **a)** oxychlorination and **b)** oxybromination of propane over CeO_2. The dashed grey lines denote the yield of product *j* and the different symbols refer to the reaction temperature.

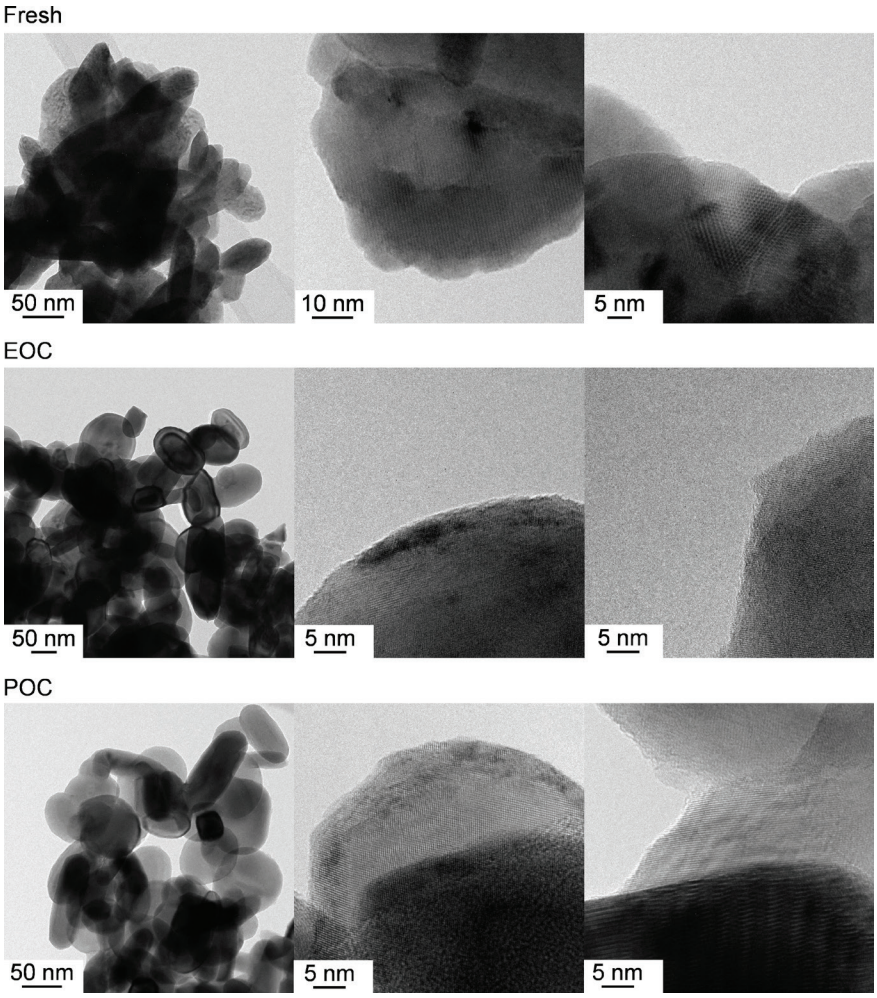

Fig. S5 High-resolution transmission electron micrographs of the fresh EuOCl catalyst and after the oxychlorination of ethane (EOC) and propane (POC).

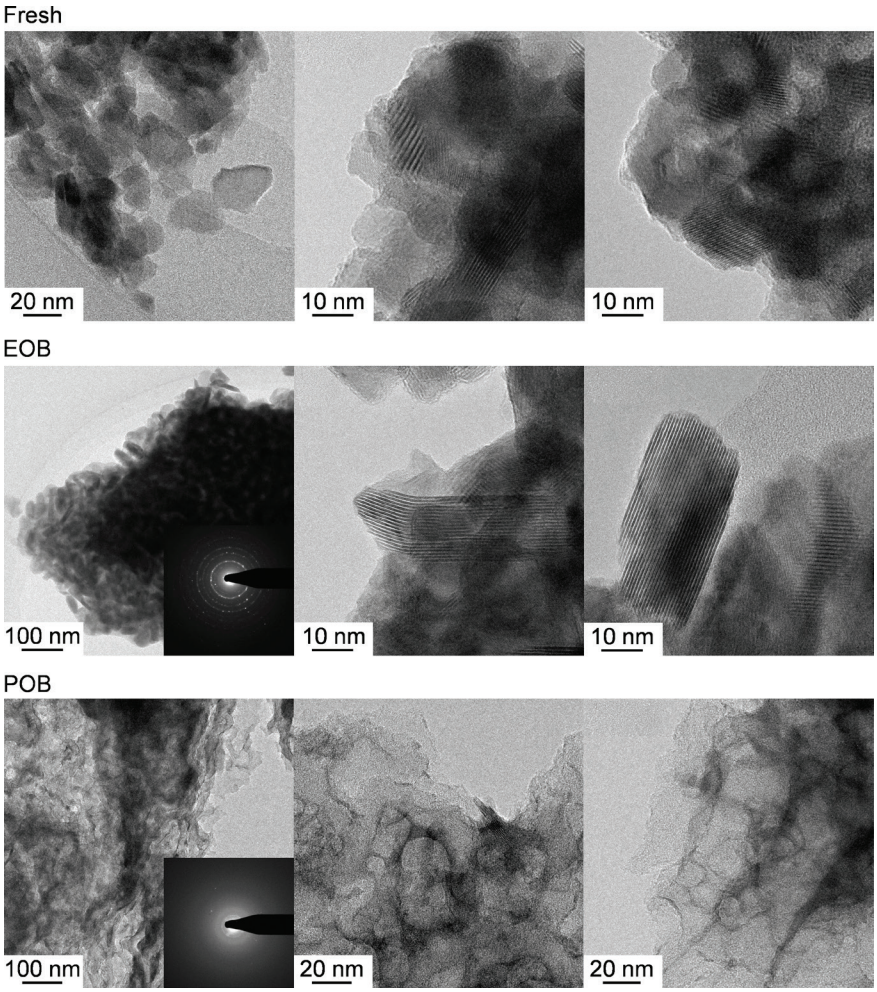

Fig. S6 High-resolution transmission electron micrographs of the fresh EuOBr catalyst and after the oxybromination of ethane (EOB) and propane (POB).

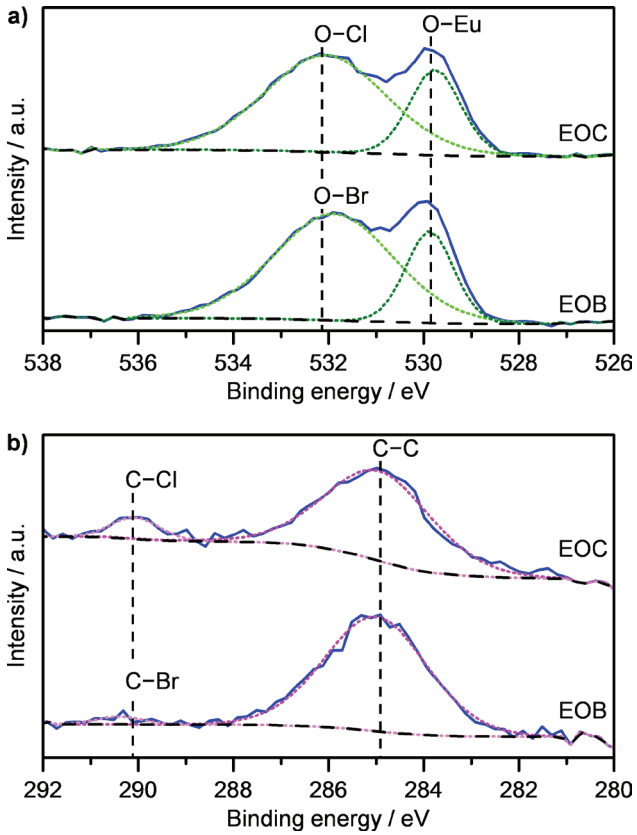

Fig. S7 a) O 1*s* and **b)** C 1*s* core level spectra of the EuOCl and EuOBr catalysts after ethane oxychlorination (EOC) and oxybromination (EOB), respectively. The solid, dashed, and dotted lines represent the raw data, background, and fits of the different contributions, respectively.

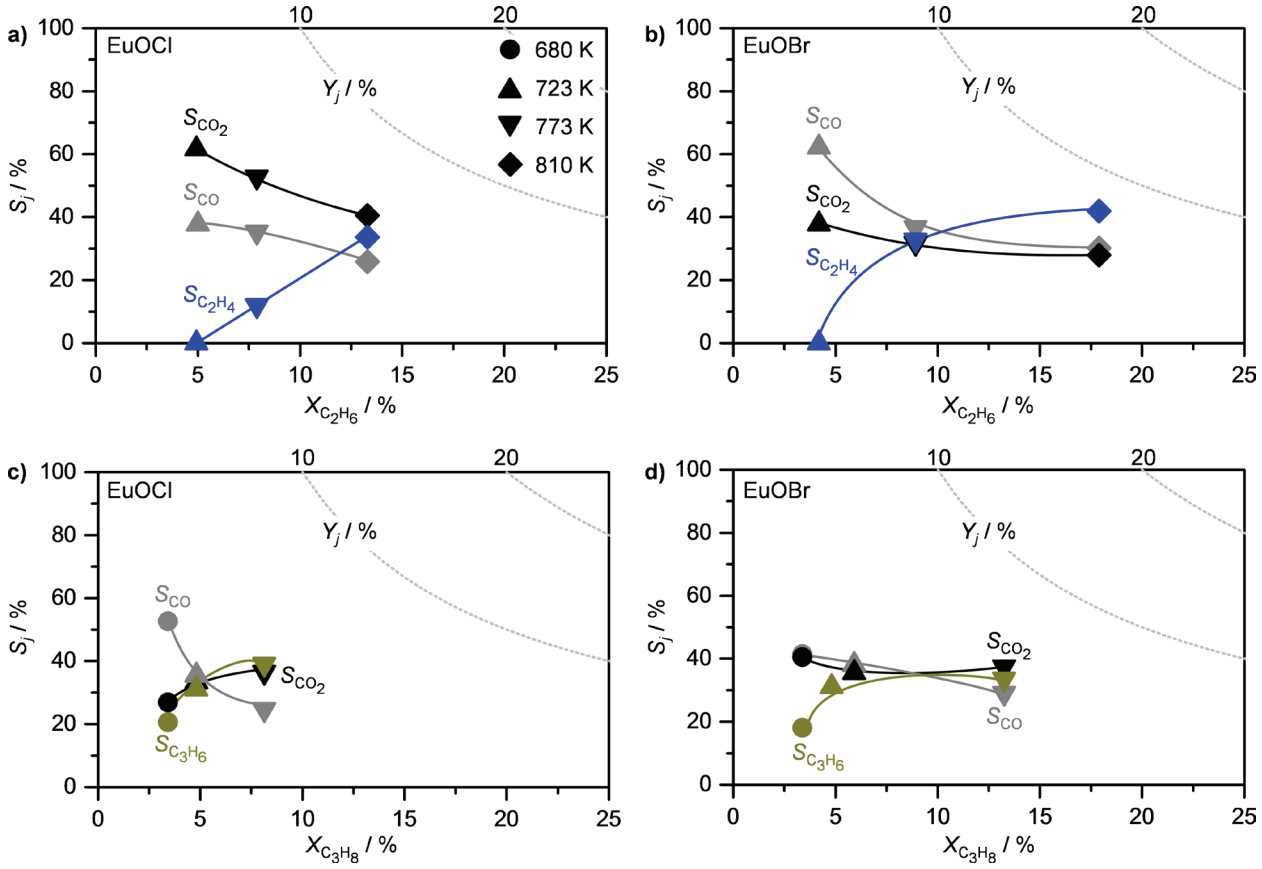

Fig. S8 Selectivity to product *j* as a function of the alkane conversion in the oxidative dehydrogenation of ethane (**a**, **b**) and propane (**c**, **d**) over the catalysts. The dotted grey lines denote the yield of product *j* and the different symbols refer to the reaction temperature.

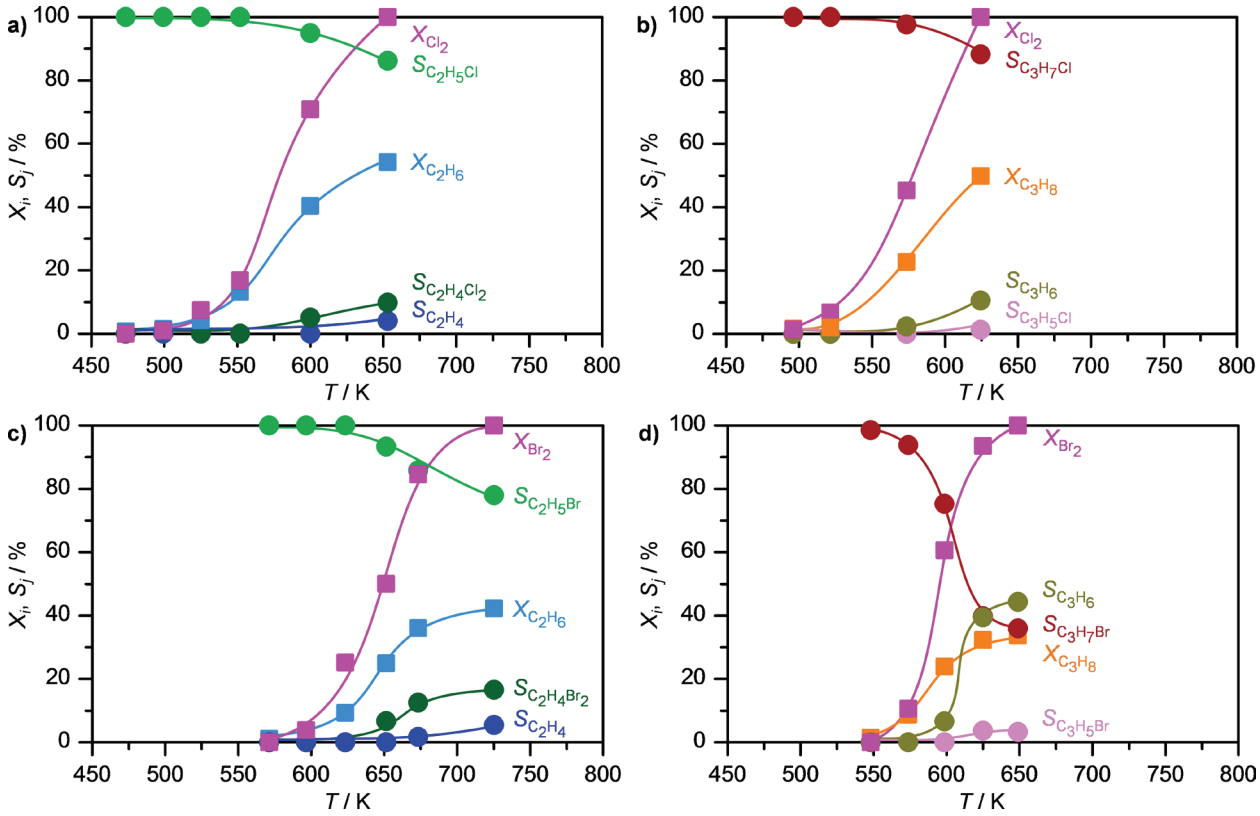

Fig. S9 Reagent conversion and product selectivity in the gas-phase chlorination of **a)** ethane and **b)** propane and in the bromination of **c)** ethane and **d)** propane.

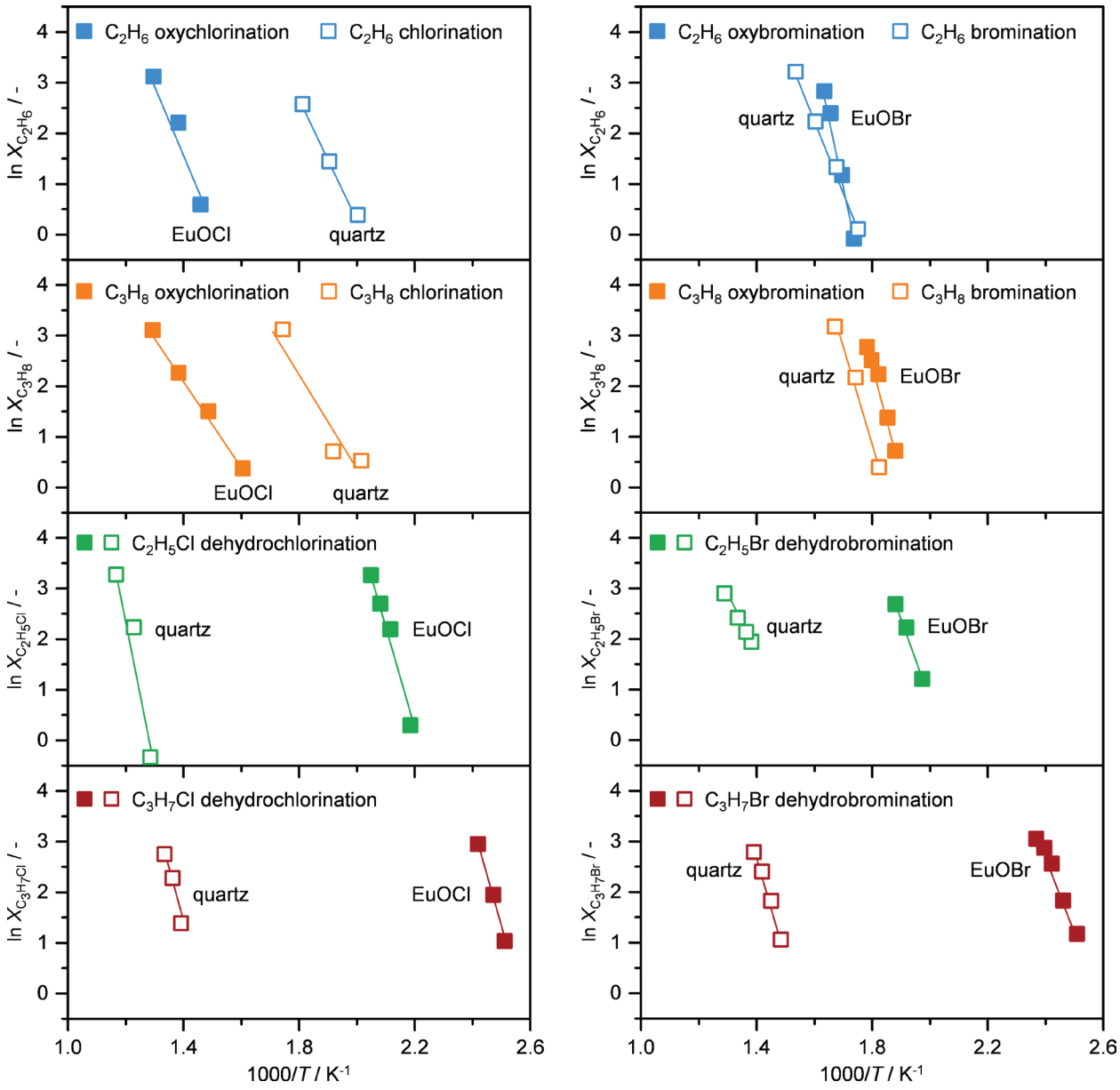

Fig. S10 Arrhenius plots of the different reactions investigated in this study.

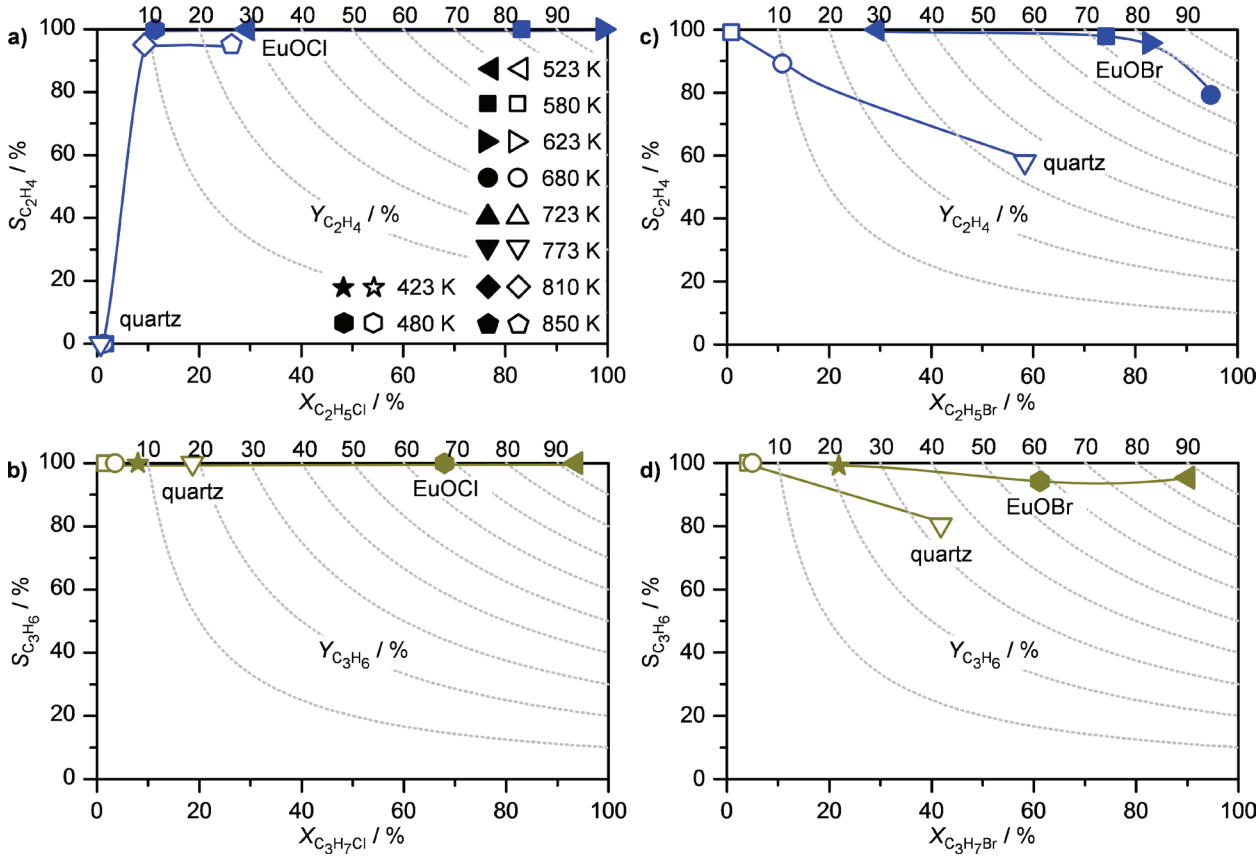

Fig. S11 Selectivity to product *j* as a function of the alkyl halide conversion in the dehydrochlorination of **a)** C_2H_5Cl and **b)** C_3H_7Cl and in the dehydrobromination of **c)** C_2H_5Br and **d)** C_3H_7Br over the catalysts (solid symbols) and over inert quartz particles (open symbols). The dotted grey lines denote the yield of product *j* and the different symbols refer to the reaction temperature.

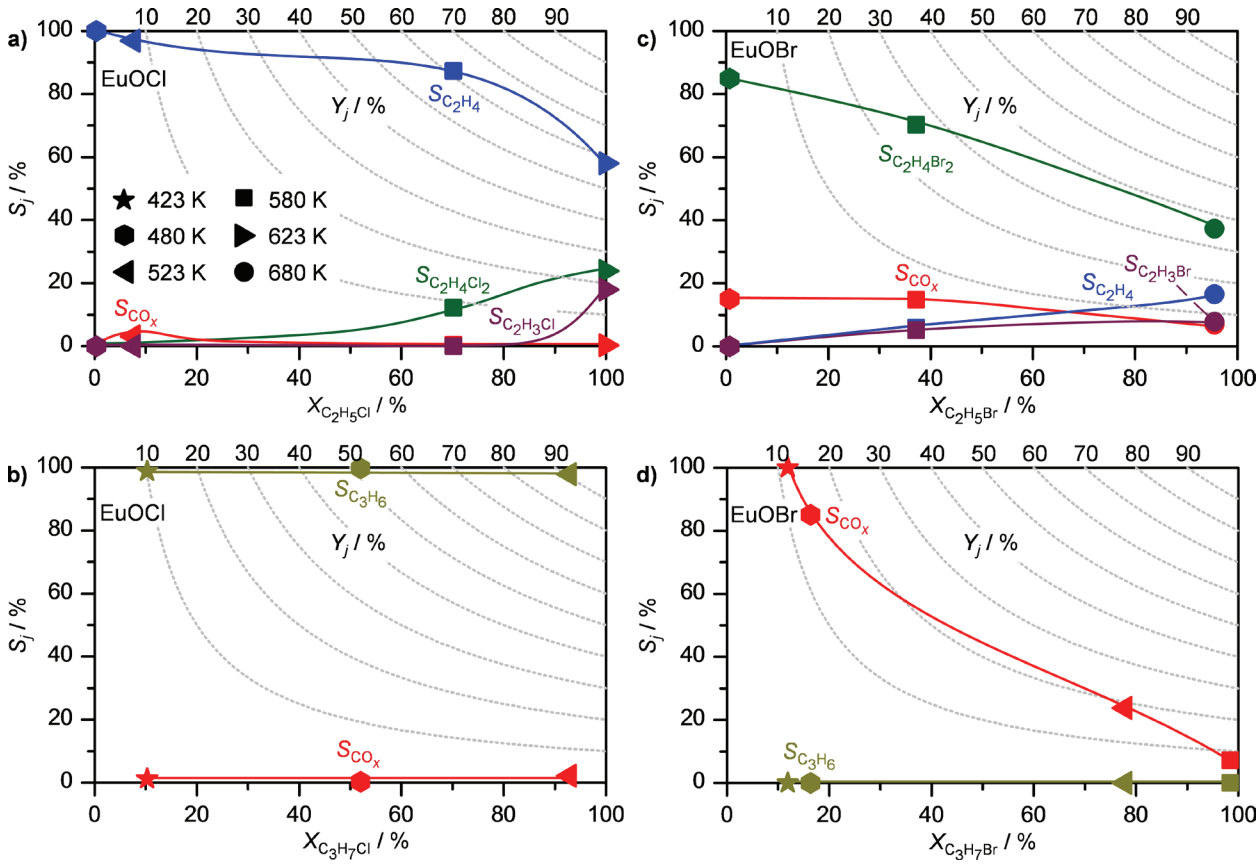

Fig. S12 Selectivity to product *j* as a function of the alkyl halide conversion in the dehydrochlorination of **a)** C_2H_5Cl and **b)** C_3H_7Cl and in the dehydrobromination of **c)** C_2H_5Br and **d)** C_3H_7Br over the catalysts in the presence of HX and O_2. The dotted grey lines denote the yield of product *j* and the different symbols refer to the reaction temperature.

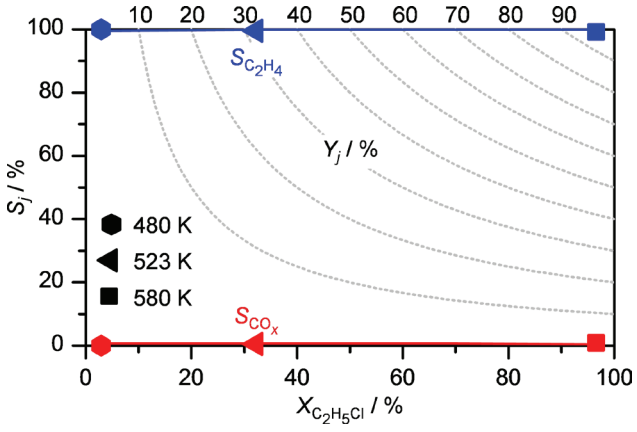

Fig. S13 Selectivity to product *j* as a function of the alkyl halide conversion in the dehydrochlorination of C_2H_5Cl over EuOCl in the presence of O_2. The dotted grey lines denote the yield of product *j* and the different symbols refer to the reaction temperature.

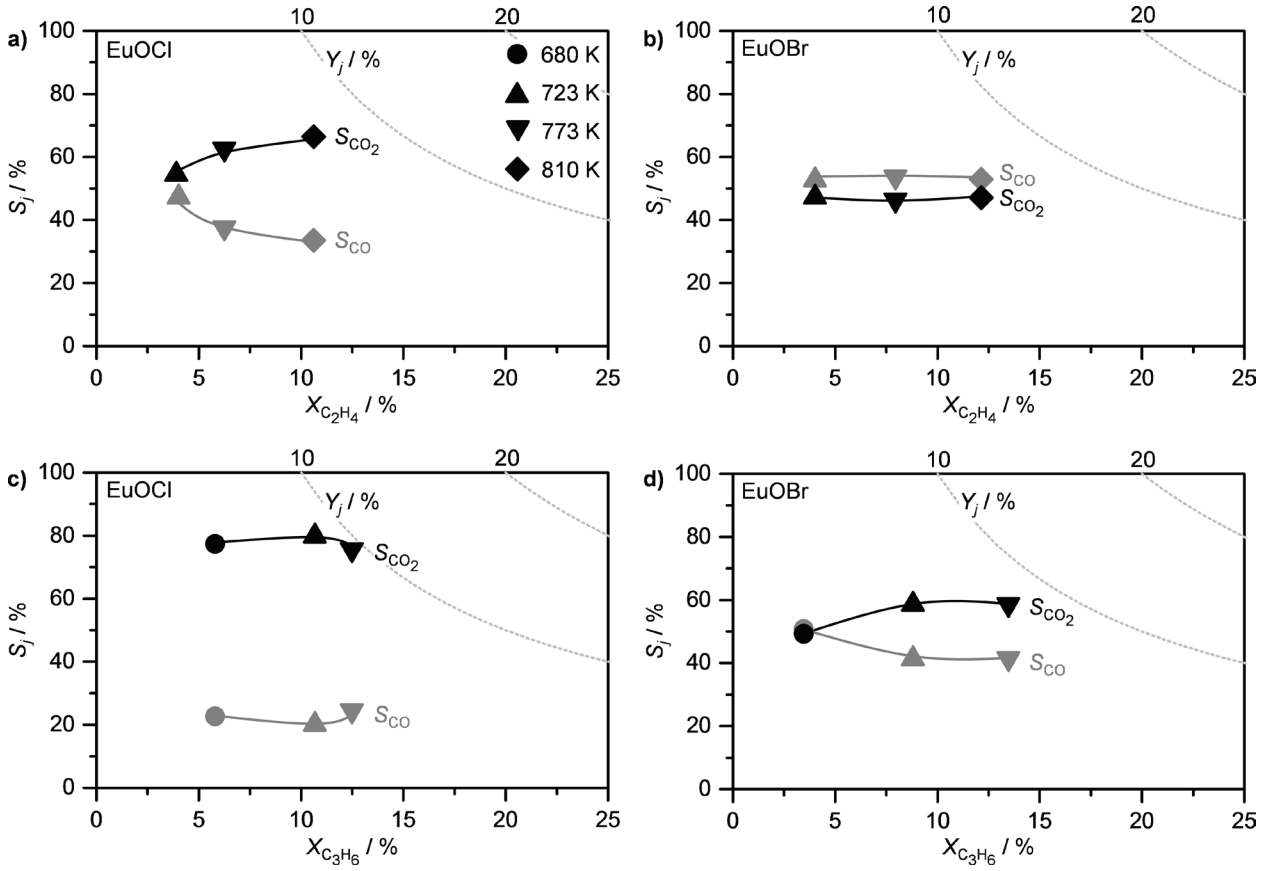

Fig. S14 Selectivity to carbon oxides as a function of the olefin conversion in the oxidation of **a**, **b)** C_2H_4 and **c**, **d)** C_3H_6 over the catalysts. The dotted grey lines denote the yield of product *j* and the different symbols refer to the reaction temperature.